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$ZnGa_2S_4$, F. W. = 333.07, tetragonal $I\bar{4}2m$, a = 5.2744(7), c = 10.407(1) Å, V = 289.51(9) Å^3, Z = 2, D_x = 3.82 g/cm^3, λ (Mo Kα) = 0.71069 Å, μ = 146.78 cm^{-1}, F(000) = 312, 19° C. $ZnGa_2S_4$ crystallizes in the defect stannite structure which is related to sphalerite. Refinement of different models of cation distribution gave R values of 0.041 to 0.043 for 360 independent reflections with $|F_o| > 3\sigma(F)$. Of the models considered, the ordered model with Zn only at point set 2a and Ga only at point set 4d was found to be worse, statistically, than models with some degree of cation disorder. Models with cation disorder are consistent with a previous review in which it was suggested that the displacement of the anion from the ideal (1/4, 1/4, 1/8) was insufficient in $ZnGa_2S_4$ to indicate cation ordering. Disorder amongst the cation sites is also consistent with reported Raman and photoluminescence results. The slight difference observed between the metal-sulfur bond lengths for the two crystallographic cation sites is attributed to the differing effect of the vacancy on these sites rather than to cation ordering.

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CRYSTAL STRUCTURE OF $ZnGa_2S_4$, A DEFECT SPHALERITE-DERIVATIVE

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ABSTRACT

$ZnGa_2S_4$, F.W. = 333.07, tetragonal $I\bar{4}2m$, a = 5.2744(7), c = 10.407(1) Å, V = 289.51(9) $Å^3$, Z = 2, D_X = 3.82 g/cm^3, λ(Mo Kα) = 0.71069 Å, μ = 146.78 cm^{-1}, F(000) = 312, 19°C. $ZnGa_2S_4$ crystallizes in the defect stannite structure which is related to sphalerite. Refinement of different models of cation distribution gave R values of 0.041 to 0.043 for 360 independent reflections with $|F_o|$ > 3σ(F). Of the models considered, the ordered model with Zn only at point set 2a and Ga only at point set 4d was found to be worse, statistically, than models with some degree of cation disorder. Models with cation disorder are consistent with a previous review in which it was suggested that the displacement of the anion from the ideal (1/4, 1/4, 1/8) was insufficient in $ZnGa_2S_4$ to indicate cation ordering. Disorder amongst the cation sites is also consistent with reported Raman and photoluminescence results. The slight difference observed between the metal-sulfur bond lengths for the two crystallographic cation sites is attributed to the differing effect of the vacancy on these sites rather than to cation ordering.

INTRODUCTION

Non-oxide inorganic compounds such as ternary sulfides and phosphides are of interest as possible infrared-transmitting window materials. $ZnGa_2S_4$ is of interest in second-phase toughening studies of ZnS (Zhang, Chen, Dunn, & Ardell, 1988) and exhibits long-wavelength infrared transparency comparable to that of ZnS (Wu, He, Dwight, and Wold, 1988; Gao, Wu, Kershaw, Dwight, and Wold, 1989).

The title compound was first reported by Hahn, Frank, Klingler, Stoerger, & Stoerger (1955). Hahn, et al (1955) postulated that the structure of $ZnGa_2S_4$ was that of an ordered defect sphalerite, the ordering of the vacancy and the two different cations giving rise to two possible structural arrangements, A and B, Figure 1. These two arrangements cannot be distinguished by X-ray powder diffraction since the scattering factors for Zn and Ga are nearly identical. In the parent AX sphalerite structure each cation is tetrahedrally bonded to four anions and each anion is tetrahedrally bonded to four cations. The relationship between the sphalerite structure and the possible zinc thiogallate structures can be seen in Figure 1. The (cubic) sphalerite cell has been doubled in one direction for ease of comparison to the thiogallate cell. In the thiogallate structure one-quarter of the cations have been removed from the sphalerite structure in an ordered fashion, lowering the symmetry to tetragonal. This results in equivalent anion sites, each coordinated by one vacancy and three cations, while pseudo-

tetrahedral coordination about each of the metal sites is preserved. The thiogallate structure has been considered as an ABX_2 defect chalcopyrite or defect stannite structure; the chalcopyrite and stannite structures are themselves ordered (tetragonal) versions of sphalerite but without vacancies. In the parent "ideal" sphalerite the anion would be at (x,y,z) coordinates $(1/4,1/4,1/4)$ or at $(1/4,1/4,1/8)$ in a cell doubled in c. In these sphalerite derivatives, the cations and vacancies occupy special positions; the anion position is specified by two or three coordinates, x,x,z or x,y,z, that determine all of the metal-sulfur and vacancy-sulfur distances.

Despite the ease of growing crystals of $ZnGa_2S_4$ by iodine transport (Nitsche, Boelsterli, & Lichtensteiger, 1961), a full single-crystal structure determination had not been reported, to our knowledge, when we initiated this structure determination. We have become aware of the single-crystal structural work of Kramer, Hirth, Hofherr, Trah (1987) and Solans, et al (1988) in which $I\bar{4}$ was proposed as the space group for $ZnGa_2S_4$. Garbato, Ledda, and Rucci (1987) point out that the crystallographic data for AB_2X_4 compounds is somewhat confused, in many cases due to similarity in atomic scattering factors, and that the correct symmetries have not always been unequivocally determined. In $I\bar{4}$ the four possible cation/vacancy sites all have the same site symmetry, $\bar{4}$; hence, regardless of the position of the vacancy an origin transformation will give an equivalent structure. In addition, due to the nearly equivalent scattering of Zn and Ga,

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in space group $I\bar{4}$ there will be nearly equivalent atoms at point sets 2c and 2d, which, if combined, are point set 4d in $I\bar{4}2m$. The differences in intensities between the space groups $I\bar{4}$ (Laue symmetry 4/m) and $I\bar{4}2m$ (Laue symmetry 4/mmm) will be due only to slight differences in the nearly-equal scattering between Zn and Ga and by movement of the sulfur away from x,x,z in $I\bar{4}2m$ to x,y,z in $I\bar{4}$, reducing the site symmetry about the vacancy and one cation site from $\bar{4}$2m to $\bar{4}$. The position of the vacancy is not the Laue-symmetry-determining factor. If Zn and Ga are completely disordered on the cation sites, then movement of the S away from x,x,z to x,y,z would be the only Laue-symmetry-determining factor. Since our preliminary report (Kipp, Lowe-Ma, Vanderah, 1989), Carpenter, Wu, Gao, & Wold (1989), hereafter abbreviated CWGW, provided us with the results of their recent structure determination of $ZnGa_2S_4$. In contrast to the earlier reports, the work of CWGW, as well as that reported here, indicate space group $I\bar{4}2m$ for $ZnGa_2S_4$.

EXPERIMENTAL

A modified version of the procedure of Nitsche, et al (1961), was used to grow transparent, colorless $ZnGa_2S_4$ crystals with tetrahedron-like morphology from polycrystalline $ZnGa_2S_4$ using iodine as the transport agent. In one end of an evacuated silica ampule (1.0 cm I.D. x 19 cm long) 0.33 g $ZnGa_2S_4$ and 5-8 mg I_2 were placed. For the first 16 h, the temperature of the deposition end of the ampule (T_d) was held at 960°C, 50-75°C

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higher than that (T_S) of the charged end. The gradient was then reversed and T_S was held at 960°C for 4 d, followed by air-quenching of the ampule. Fused masses of colorless tetrahedra, some 2-3 mm on an edge, were obtained as well as smaller separate crystals suitable for X-ray diffraction studies. The metal stoichiometry of the crystals as found by ICP emission analysis, 1.00 Zn : 2.00 Ga (±0.05), was consistent with the expected composition. From a preliminary investigation of the ZnS-Ga$_2$S$_3$ phase diagram, White (1980) concluded that there was no evidence for a solid-solution (variation of the Zn:Ga ratio) and that ZnGa$_2$S$_4$ exists as a line compound between 900° and 1100°C. Zhang, et al (1988) also reported seeing only one phase at 900° for 1:1 ZnS:Ga$_2$S$_3$. This is in agreement with elemental analyses of our crystals which indicated no appreciable non-stoichiometry. The X-ray powder diffraction pattern of our crystals matched that reported for tetragonal ZnGa$_2$S$_4$ (Gates, 1976; Hahn, et al, 1955).

A crystal of 0.22 mm on an edge was used for data collection. The unit cell parameters were determined by a least-squares fit of 25 computer-centered reflections. The parameters for $2\theta/\theta$ data collection on a Nicolet R3 were as follows: 2θ range of 4° to 70°; all hkl with minimum-maximum hkl values of h/0 to +9/, k/0 to +9/, l/-17 to +17/ collected; 2θ scan range of $2\theta(\alpha_1)$-1.0° to $2\theta(\alpha_2)$+1.0°; ratio of total background counting time to scan time of 1.0; variable 2θ scan speeds of 4° to 12°; three check reflections, (112), (008), and (440), collected every 93 reflections with check reflection variation of about ±5%

during data collection. The only observed systematic absences

were h+k+l=2n+1 indicating a body-centered tetragonal cell

without any additional elements of translational symmetry. Data

reduction included Lorenz and polarization corections as well as

numerical absorption corrections (SHELXTL, 1984) for a tetragonal

dispenoid with faces {$\bar{1}12$}. Minimum and maximum transmission

values were 0.161 and 0.282, respectively. The location of

mirror planes on preliminary X-ray precession alignment

photographs relative to the external morphology of three

tetrahedron-like crystals of $ZnGa_2S_4$ clearly showed that the

crystals were, indeed, tetragonal dispenoids (tetragonal

tetrahedrons). Laue photographs exhibited Laue symmetry 4/mmm.

After corrections the 1600 observations were merged in $I\bar{4}2m$

(R_{merge} = 0.042) to give 363 unique reflections, 360 with $|F_o|$ >

$3\sigma(F)$. Data were also merged in $I\bar{4}$ (R_{merge} = 0.063) and

reflections that would be equivalent in $I\bar{4}2m$ were checked for

true equivalence, which they appeared to be. A sharpened

Patterson map exhibited peaks at (u,v,w) coordinates of (0,0,0),

(1/2,0,1/4), (1/2,1/2,0), and (0.2567, 0.2567, 0.1275).

Refinement was initiated with the following atomic (x,y,z)

coordinates: Zn (0,0,0), point set 2a; Ga (0,1/2,1/4), point set

4d; S (x=y=0.2567, 0.1275), point set 8i. In our preliminary

communication (Kipp, Lowe-Ma, Vanderah, 1989) we reported a model

(R = 0.043) with Ga fully occupying point set 4d, S fully

occupying point set 8i, variable Zn occupancy at (0,0,0) with

5.6% more "Zn" than expected, and 1.8% "Zn" at the vacancy site

(0,0,1/2) (point set 2b). However, 1.8% "Zn" at (0,0,1/2) is an amount only twice that of the esd for the site occupancy factor of that position. As suggested to us by R. E. Marsh, equally reasonable models might be with the "Zn" at (0,0,1/2) eliminated and mixing between the Zn and Ga sites allowed.

After completion of refinement of a model with mixing of Zn and Ga at the two cation sites, the structure determination of CWGW became available to us. They reported in their structure determination a model with Ga at (0,0,0), point set 2a; 0.5Ga + 0.5Zn at (0,1/2,1/4), point set 4d; and S in point set 8i. For stoichiometric $ZnGa_2S_4$ in $I\bar{4}2m$ the cation distribution could be modelled in four ways: (I) Zn at point set 2a and Ga at point set 4d with no disorder; (II) that of CWGW with Ga at point set 2a and 0.5Zn + 0.5Ga disordered on point set 4d; (III) complete disorder with 1/3Zn + 2/3Ga at point set 2a as well as at point set 4d; (IV) a disordered model intermediate and variable between II and III. Least-squares refinements of the four models was by minimization of $[\Sigma w(|F_o|-k|F_c|)^2]$ with $w = 1/[\sigma^2(F) + 0.0008F^2]$ (SHELXTL, 1984) using neutral-atom scattering factors (International Tables, 1974). A single temperature factor was used for each site, even those with disordered occupancy. A parameter for extinction was included in the refinement. Refinement of model I converged for 12 parameters (max.shift/esd of 0.001) with $R = 0.043$, $wR = [\Sigma w(|F_o|-k|F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}} = 0.045$, GOF = 1.35, slope of normal probability plot = 1.20. Refinement of model II converged for 12 parameters (max.shift/esd

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of 0.000) with R = 0.041, wR = 0.041, GOF = 1.24, slope of normal probability plot = 1.03. Refinement of model III converged for 12 parameters (max.shift/esd of 0.000) with R = 0.041, wR = 0.042, GOF = 1.26, slope of normal probability plot = 1.06. For model IV, the amount of Zn (and Ga) at each site was allowed to vary with the total occupancy constrained to be 1, although the total Zn:Ga stoichiometry could not be constrained to be 1:2. Starting from 1/3Zn + 2/3Ga at both point set 2a and point set 4d, model IV with 14 parameters refined to R = 0.041, wR = 0.041, GOF = 1.24, and slope of normal probability plot = 1.04. However, the resulting occupancies, 34% Zn + 66% Ga (±12%) at point set 2a and 24% Zn + 76% Ga (±12%) at point set 4d, did not truly converge (max.shift/esd of 0.4); the large esd's on the occupancy indicate that a true minimum may not exist due to the similarity in Zn and Ga scattering.

Refinement of the X-ray diffraction data indicates that an unambiguous choice between models II, III, and IV is not possible, although the statistically worse refinement of model I suggests that a structure with completely ordered cations can be ruled out. In the absence of neutron diffraction studies of $ZnGa_2S_4$, the choice of the most chemically reasonable of the remaining models depends on consideration of crystal-chemical arguments and the results of other types of experiments. Accordingly, as discussed below, we conclude that the most chemically reasonable model is III, with essentially complete, or nearly so, cation disorder between the 2a and 4d point sets. The

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atomic coordinates, thermal parameters, and bond lengths and angles for model III are given in Table 1.[1]

DISCUSSION

In the study by CWGW the choice of model II with Ga in point set 2a and ½Ga + ½Zn disordered in point set 4d was largely predicated on the observation of a slightly shorter metal-sulfur bond length about point set 2a, 2.281(1)Å vs 2.315(1)Å about point set 4d. Our interest in the reasonableness of this assumption was piqued by considering the possible reasons for cation disorder on only one of the tetrahedral cation sites. Unlike the spinel system, in which the well-known "normal" and "inverse" forms involve cation exchange and order-disorder across tetrahedral and octahedral sites, the two cation sites in $ZnGa_2S_4$ are coordinatively very similar. The Ga-S bond length calculated from the defect sphalerite form of Ga_2S_3 is 2.24 Å and the Zn-S bond length in sphalerite is 2.342 Å. These bond lengths suggest that in $ZnGa_2S_4$, with cation-sulfur bond lengths, as observed in the present study, of 2.288(1) and 2.312(1) Å (for the distances from point set 2a to S and from point set 4d to S, respectively), there is mixing of Zn and Ga on both of the cation sites, which

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1. Lists of structure factors for model III have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP _____ (____pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

favors a model with at least some disorder across point sets 2a and 4d. If Ga-S and Zn-S bond lengths were well-known and constant in similar structures, then the difference in bond lengths in $ZnGa_2S_4$ might indicate the relative populations of Zn and Ga on the two sites. This is not the case, however; observed variations in Zn-S and Ga-S distances in tetrahedral coordination are as large as the differences observed in $ZnGa_2S_4$. A summary of Ga-S distances in compounds containing GaS_4 tetrahedra is presented in Table 2. For a Zn-S bond length Shannon's ionic radii would predict 2.34 Å, the same bond length as observed in sphalerite. However, Shannon (1981) noted large deviations (up to 0.04 Å) for mean Zn-S bond lengths. From quantum-mechanical considerations rather than a hard-sphere model, Van Vechten and Phillips (1970) developed a table of additive covalent radii for tetrahedrally-bonded (diamond, sphalerite, wurtzite) structures and concluded that Zn and Ga have the same covalent radii (1.225 Å) and, hence, identical bond lengths (2.352 Å) in tetrahedrally-bonded structures.

For model II, the occupation of point set 2a solely by the higher valent Ga atoms is not consistent with the observed bond angles about the two cation sites in $ZnGa_2S_4$. As noted by Shay and Wernick (1975) structural distortions in chalcopyrite-type compounds are driven by a tendency to form more ideal tetrahedra about the higher-valent cation, with accommodating distortions of the tetrahedra about the lower-valent species. In $ZnGa_2S_4$ the anion tetrahedron about site 2a is significantly more distorted,

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with four angles of 107.1° and two of 114.4(1)°, than the anion tetrahedron about site 4d, with four angles of 110.4° and two angles of 107.7°. This would suggest that Zn is predominantly at the 2a site (0,0,0) since it displays the more distorted tetrahedral coordination, in apparent contradiction to the shorter cation-anion bond length observed for this site.

The crystal-chemical effects of the vacancy (at point set 2b) upon the cation sites 2a and 4d are different, however, and could reasonably cause the observed differences in bond lengths and bond angles even in the complete absence of cation ordering. Two unit cells for the $ZnGa_2S_4$ structure ($I\bar{4}2m$) are illustrated in Figure 2. The structure can be viewed as alternating planes of metals/vacancies and sulfurs along the c-axis. The vacancies (point set 2b) are co-planar with metals at point set 2a; in contrast, all of the cation sites are fully occupied in the plane of metals at point set 4d. Thus, the crystal-chemical effects of the vacancy should be most pronounced in the sulfur-metal/vacancy (2a,2b)-sulfur slab of the structure. The z-coordinates of the sulfur planes are given in Fig. 2 along with the ideal values in parentheses. Relative to the ideal z-coordinates, the sulfur layers shift slightly toward the 2a/2b metal/vacancy plane, decreasing the metal-sulfur and vacancy-sulfur distances and leading to more highly distorted coordination polyhedra within this structural slab. As a consequence, the sulfur planes on either side of the 4d-metal layer are pulled slightly apart, increasing the metal-sulfur bond lengths while the tetrahedra

remain more nearly ideal. The shortest distance in the structure is the distance from sulfur to the 2b vacancy site, 2.191(1) Å. The slight shifts in sulfur positions from the ideal values of (1/4,1/4,1/8) decrease the sulfur-vacancy distance, which would be 2.274 Å if the sulfurs were at the ideal coordinates. The apparent tendency of the structure to collapse around the vacancy site might be attributable to incipient sulfur-sulfur interactions that predominate over any lone-pair effects (even though $ZnGa_2S_4$ is colorless). The closest observed S-S contacts in the structure range from 3.560 to 3.843 Å. The shortest S-S distances, two at 3.560 and two at 3.616 Å, do indeed occur in the pseudo-tetrahedron about the vacancy. These S-S distances are shorter than those observed in ZnS (3.82 Å) and completely randomized sphalerite-type Ga_2S_3 (3.66 Å). In monoclinic alpha-Ga_2S_3, with ordered vacancies, shrinkage about vacancies was also noted by Goodyear and Steigmann (1963). Thus, collapse of the structure about the cation vacancy causes slightly shorter bond lengths to and a more distorted tetrahedran about the cation 2a site; assumption of higher Ga content at this site is, therefore, unnecessary.

Garbato, Ledda, and Rucci (1987) have recently reviewed structural distortions in ABX_2 and AB_2X_4 tetrahedrally-bonded compounds and suggest, based on the available crystallographic information, that the axial c/a ratio as well as the internal distortion of anion displacement away from the ideal (1/4,1/4,1/8) can be used to predict cation and/or vacancy

disorder. A c/a ratio near 2.0 indicates little internal distortion and, if not at room temperature, then probable cation disorder at higher temperatures. The observed c/a ratio for $ZnGa_2S_4$ is 1.97, suggesting cation disorder. As defined by Garbato, et al (1987), the anion distortion is $\sigma_O = [(x-0.25)^2 + (y-0.25)^2 + (z-0.125)^2]^{\frac{1}{2}}$. Based on their review of known structures, a σ_O value of 0.0145(5) defines a critical value dividing structures into two classes, those that are ordered, $\sigma_O > 0.0145$, and those that are disordered, $\sigma_O < 0.0145$. Our refinement results for $ZnGa_2S_4$ yield a σ_O value of 0.0123 which suggests cation disorder. These predictors, as well as a statistically worse least-squares refinement of an ordered cation distribution, are in complete agreement with the prediction by Garbato, et al (1987) that $ZnGa_2S_4$ should be disordered. The related compound $CdGa_2S_4$ has been found to be ordered in space group $I\bar{4}$ with Ga in the same layer as the vacancy; in the other layer the Cd and Ga are ordered in different sites (Krämer, Frick, and Siebert, 1983). From the structural data given by Krämer, et al (1983), the σ_O value for $CdGa_2S_4$ is 0.0146. The larger size of Cd and the differences in its bonding relative to that of Zn apparently force distortion of the anion array and ordering of the cations.

The results of spectroscopic studies provide additional support for our conclusion that the most chemically reasonable structural model for $ZnGa_2S_4$ is III, with complete, or nearly so, cation disorder across the 2a and 4d sites. Raman spectral

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studies of $ZnGa_2S_4$ (White, 1980; Razzetti, Lottici, and Antonioli, 1987) revealed broad bands indicative of structural disorder. These results are consistent with similar studies of $Cd_{1-x}Zn_xGa_2S_4$ (Razzetti, Lottici, and Antonioli, 1987), in which it was observed that ordering decreased with increasing Zn content. Recently, photoluminescence spectra of $ZnGa_2S_4$ have been interpreted as indicating cation disorder (Derid, et al, 1989).

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CAPTIONS

Figure 1: Comparison of the cubic AX sphalerite structure (two
cells shown) with the possible ordering arrangements A and B.
Large open circles represent anions and each set of small circles
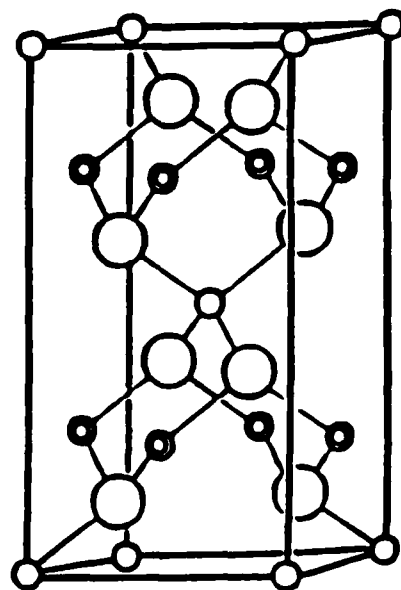represents a crystallographic point set for the cation sites.

Figure 2: Two unit cells of the $ZnGa_2S_4$ ($I\bar{4}2m$) structure with
(ideal) and observed z-coordinates of the sulfur atoms.
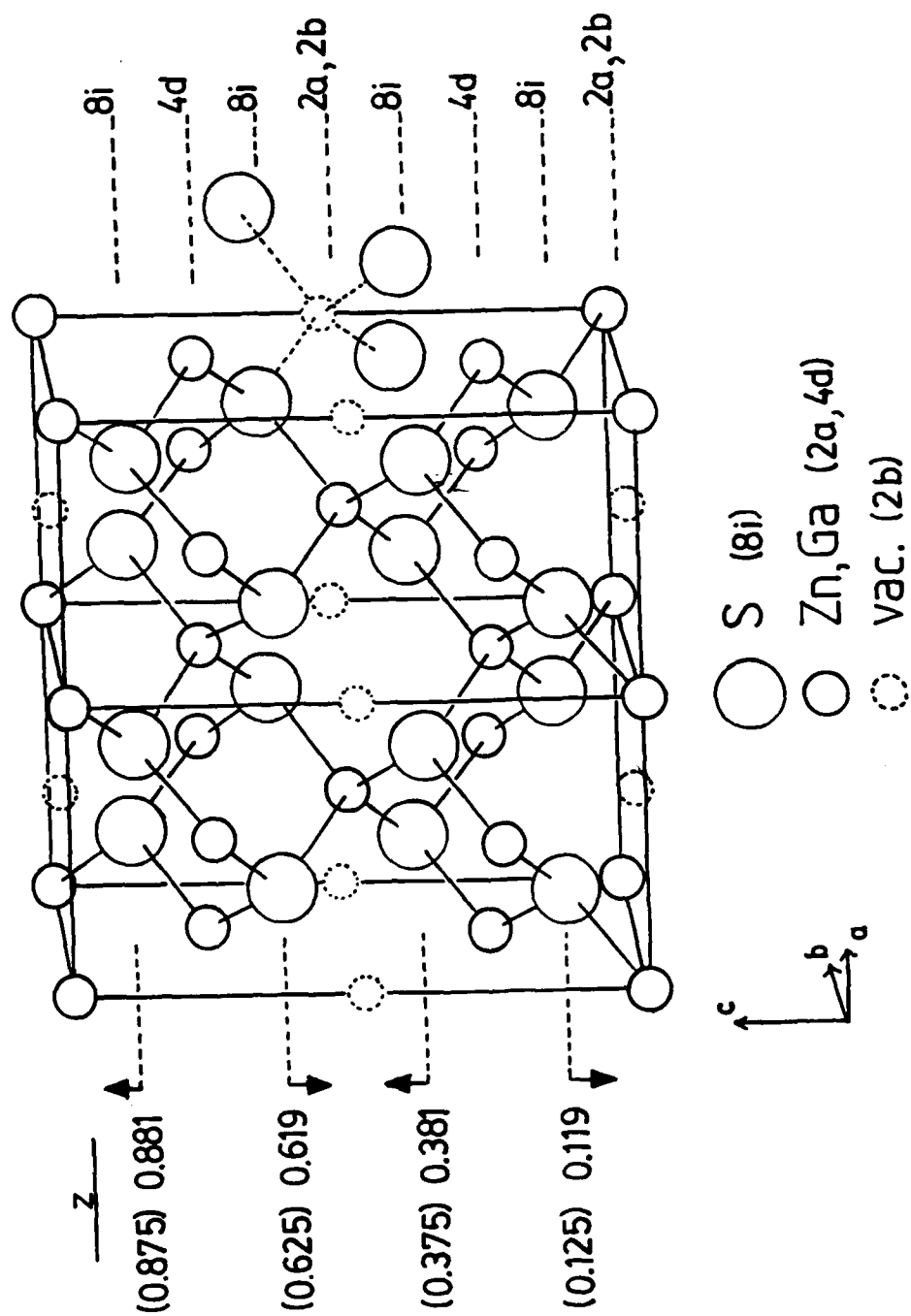
AX

⊘ A
○ X

I$\bar{4}$

I$\bar{4}$2m

A
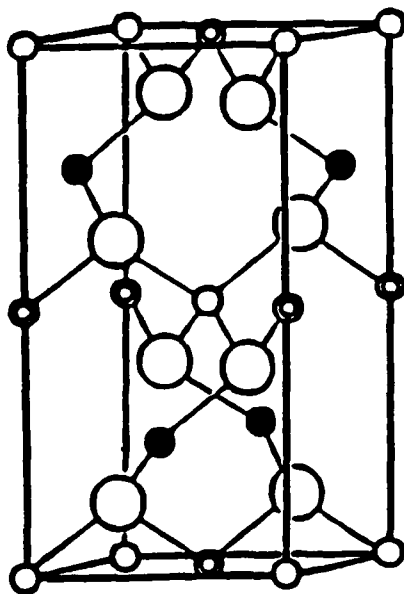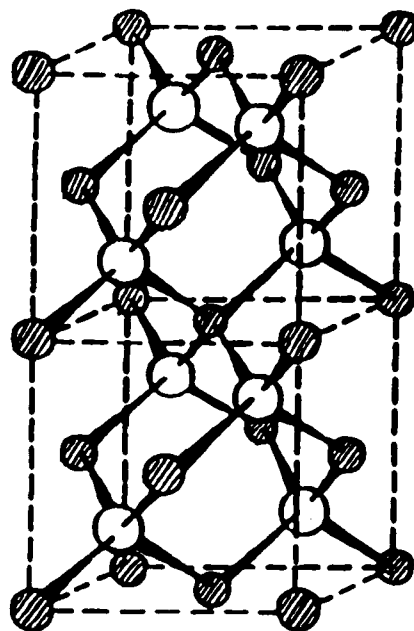
B

Figure 1.

Figure 2.

Table 1. Atomic coordinates, thermal parameters*, bond lengths and angles for model III.

atom	x	Y	z	occup.	U_{11}	U_{33}	U_{23}	U_{12}	U_{eq}
Zn(1)/Ga(2)	0.0	0.0	0.0	0.333/0.667	.0114(3)	.0081(4)	.0	.0	.0103(2)
Zn(2)/Ga(1)	0.0	0.50	0.25	0.333/0.667	.0110(3)	.0110(4)	.0	.0	.0110(2)
S	0.25761(14)	x	0.11902(9)	1.0	.0112(4)	.0094(5)	-.0009(2)	.0007(2)	.0106(2)

bond lengths: point set 2a to sulfur, 2.288(1) Å
point set 4d to sulfur, 2.312(1) Å

bond angles: about point set 2a; 4 x 107.1°, 2 x 114.4(1)°
about point set 4d; 4 x 110.4°, 2 x 107.7°
about sulfur; 2 x 107.4°, 107.6°

*The anisotropic thermal parameters are of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12})]$ in Å².
U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 2. Representative Ga-S bond lengths.

Compound	Range, Å	Reference
$CaGa_2S_4$ [a]	2.252 – 2.297	Eisenmann, et al (1983)
$SrGa_2S_4$ [a]	2.244 – 2.335	Eisenmann, et al (1983)
$YbGa_2S_4$ [a]	2.241 – 2.282	Guseinov, et al (1983)
$EuGa_2S_4$ [a]	2.237 – 2.311	Roques, et al (1979)
$Ga_{1.33}Cr_4S_8$ [b]	2.292, 2.242	Ben Yaich, et al (1983)
$GaMo_4S_8$ [b]	2.275	Ben Yaich, et al (1983)
$Ca_2La_2Ga_6S_4$	2.196 – 2.285	Mazurier, et al (1987)
α-Ga_2S_3 monoclinic [c]	2.18 – 2.32	Goodyear & Steigmann (1963)
hexagonal [c]	2.07 – 2.38	Tomas, et al (1987)
β-Ga_2S_3	2.251 – 2.269	Tomas, et al (1987)

a isostructural compounds
b isostructural compounds
c for cation sites with partial Ga occupancy